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Molecular Orbitals: an Introduction

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A Simple Introduction to Molecular Orbitals

References

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Separation of variables

We say that a system's Hamiltonian $\hat{H}(q, Q)$ is separable if

$$\hat{H}(q, Q) = \hat{H}_q(q) + \hat{H}_Q(Q).$$

If the Hamiltonian of a system is separable, the corresponding energy eigenfunction problem can be broken up into two smaller problems. Explicitly, if

$$\begin{aligned}\hat{H}_q(q) \phi_i(q) &= \epsilon_i \phi_i(q) \\ \hat{H}_Q(Q) \psi_I(Q) &= E_I \psi_I(Q)\end{aligned}$$

then

$$\hat{H}(q, Q) \phi_i(q) * \psi_I(Q) = (\epsilon_i + E_I) \phi_i(q) * \psi_I(Q), \quad \text{all } i, I$$

and the set of functions $\{\phi_i(q) * \psi_I(Q)\}_{i,I}$ provides a basis set for functions of (q, Q) . Separable Hamiltonians are easier to diagonalize and the results are easier to comprehend.

The Born-Oppenheimer Approximation

No energy eigenvalue problem for an interesting chemical system can be solved precisely. Thus practical discussions of chemical systems always involve approximations. Usually, the approximation is to treat a system whose Hamiltonian is not separable as if it were separable.

To illustrate this, consider the simplest multi-electron molecule, H_2 . If we neglect relativistic corrections, the Hamiltonian for this molecule is

$$\hat{H} = -\frac{\hbar^2}{2M} \left[\frac{\partial^2}{\partial R_1^2} + \frac{\partial^2}{\partial R_2^2} \right] - \frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} \right] + \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{|R_2 - R_1|} + \frac{1}{|r_2 - r_1|} \right] - \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{|R_1 - r_1|} + \frac{1}{|R_1 - r_2|} + \frac{1}{|R_2 - r_1|} + \frac{1}{|R_2 - r_2|} \right] \quad (1)$$

with R_1, R_2 locating the nuclei (mass M) and r_1, r_2 locating the electrons (mass m).

There is a Coulomb interaction between every pair of particles.

With the goal of *separating* this Hamiltonian into an electronic term and a nuclear term, suppose that an energy eigenstate with energy \mathcal{E} has the form

$$\Psi(R_1, R_2, r_1, r_2) = \Phi(R_1, R_2) \psi(r_1, r_2) \quad (2)$$

Then $\hat{H} \Psi = \mathcal{E} \Psi$ can be rewritten

$$\begin{aligned} & -\frac{\hbar^2}{2m\psi(r_1, r_2)} \left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} \right] \psi(r_1, r_2) \\ & + \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{|r_2 - r_1|} - \frac{1}{|R_1 - r_1|} - \frac{1}{|R_1 - r_2|} - \frac{1}{|R_2 - r_1|} - \frac{1}{|R_2 - r_2|} \right] \\ & = \frac{\hbar^2}{2M\Phi(R_1, R_2)} \left[\frac{\partial^2}{\partial R_1^2} + \frac{\partial^2}{\partial R_2^2} \right] \Phi(R_1, R_2) - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|R_2 - R_1|} + \mathcal{E} \end{aligned} \quad (3)$$

The right hand side of this expression is independent of r_1, r_2 , but R_1, R_2 are present on the left hand side \Rightarrow A true separation of electronic and nuclear variables has not been achieved. Still, $m \ll M$ leads us to expect that the *motion* of the nuclei will have little effect on the state of the electrons. Essentially, the nuclei provide a constant external field in which the electrons move. Thus we identify an *electronic* Hamiltonian,

$$\begin{aligned} \hat{H}_{elec} = & -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} \right] \\ & + \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{|r_1 - r_1|} - \frac{1}{|R_2 - r_1|} - \frac{1}{|R_1 - r_2|} - \frac{1}{|R_2 - r_1|} - \frac{1}{|R_2 - r_2|} \right], \end{aligned} \quad (4)$$

with the understanding that the eigenvalues and eigenfunctions of \hat{H}_{elec} will depend *parametrically* on $\mathbf{R}_1, \mathbf{R}_2$,

$$\hat{H}_{elec}\psi_i(\mathbf{r}_1, \mathbf{r}_2|\mathbf{R}_1, \mathbf{R}_2) = E_i(\mathbf{R}_1, \mathbf{R}_2)\psi_i(\mathbf{r}_1, \mathbf{r}_2|\mathbf{R}_1, \mathbf{R}_2) \quad (5)$$

With a solution to (5), (3) reduces to

$$-\frac{\hbar^2}{2M} \left[\frac{\partial^2}{\partial \mathbf{R}_1^2} + \frac{\partial^2}{\partial \mathbf{R}_2^2} \right] \Phi(\mathbf{R}_1, \mathbf{R}_2) + \left[\frac{e^2}{4\pi\epsilon_0 |\mathbf{R}_2 - \mathbf{R}_1|} + E_i(\mathbf{R}_2, \mathbf{R}_1) - \mathcal{E} \right] \Phi(\mathbf{R}_1, \mathbf{R}_2) = 0$$

That is, the states of the nuclei are determined by

$$\hat{H}_{nuc} \Phi(\mathbf{R}_1, \mathbf{R}_2) = \mathcal{E} \Phi(\mathbf{R}_1, \mathbf{R}_2)$$

with

$$\hat{H}_{nuc} = -\frac{\hbar^2}{2M} \left[\frac{\partial^2}{\partial \mathbf{R}_1^2} + \frac{\partial^2}{\partial \mathbf{R}_2^2} \right] + \frac{e^2}{4\pi\epsilon_0 |\mathbf{R}_2 - \mathbf{R}_1|} + E_i(\mathbf{R}_2, \mathbf{R}_1) \quad (6)$$

|| The electronic energy provides a *potential energy* for the nuclear motion. *why?*

why? Because of the large mass difference between m and M , this separation is usually an excellent approximation. We picture the nuclei as moving (adiabatically) on a potential energy surface $E_i(\mathbf{R}_2, \mathbf{R}_1)$ – the *Born-Oppenheimer* surface* – that is actually the energy of the electrons in the molecule with fixed nuclei. Different Born-Oppenheimer surfaces are associated with different electronic states. Vibrational and rotational spectroscopy is associated with the excitation of nuclear motion on a particular Born-Oppenheimer surface. Electronic spectroscopy is associated with transitions between different Born-Oppenheimer surfaces with essentially no nuclear motion.

The Eigenfunctions of \hat{H}_{elec}

The only term in \hat{H}_{elec} that prevents us from separating this Hamiltonian into two one-electron Hamiltonians is the electron-electron repulsion term, *Coulomb?*

$$\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_2 - \mathbf{r}_1|} \quad (7)$$

* This “almost” separation approximation was introduced by M. Born and J. R. Oppenheimer in 1927.

If we neglect this term, the electronic states of H_2 will have the form

$$\psi_{ij}(\mathbf{r}_1, \mathbf{r}_2) = \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \quad (8)$$

with the $\phi_i(\mathbf{r})$ eigenfunctions of the one-electron Hamiltonian

$$\hat{H}_1 \phi_i(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2 \phi_i(\mathbf{r}) - \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{|\mathbf{r} - \mathbf{R}_1|} + \frac{1}{|\mathbf{r} - \mathbf{R}_2|} \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad (9)$$

The $E_i(\mathbf{R}_1, \mathbf{R}_2)$ of (5) is now $\epsilon_i + \epsilon_j$. [Keep in mind that $\phi_i(\mathbf{r})$ and ϵ_i depend parametrically on $(\mathbf{R}_1, \mathbf{R}_2)$.] We call the solutions to (9) the *molecular orbitals* (MO's) of H_2 . The extension to many electron atoms and molecules is straight-forward.

Note that

1. as the electrons are attracted to the nuclei and repelled by each other, we expect that

$$\left\langle \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|} \right\rangle \ll \left\langle \frac{1}{|\mathbf{r}_1 - \mathbf{R}_1|} \right\rangle, \quad \text{etc.}$$

So the neglect of the term (7) in (4) is not unreasonable. ¶

2. the removal of electron-electron interactions destroys any correlation between electrons in different orbitals. This is an approximation that is *qualitatively* unrealistic, even when it is good *quantitatively*. ¶
3. less drastic approximations can be made. We'll look at other approximations used to generate molecular orbitals later.
4. (9) can actually be solved exactly for H_2 . For any other molecule, however, this is not the case. So the actual determination of molecular orbitals always relies on additional approximations. ¶

Molecular Orbitals

All the N -dimensional energy eigenfunction problems for which explicit analytic solutions are known have Hamiltonians that can be “separated” into N one-dimensional problems. It is experience with problems of this special type that forms the basis of our image of real three-dimensional problems.

Multi-electron systems can not be separated in this way, so our experience with solvable problems does not prepare us to deal with multi-electron systems. [If we compute the electronic wave function for the two electrons in H_2 , we could only “see” the solution if we were comfortable plotting a function of six variables.] For this reason chemists always approximate real atomic and molecular systems in such a way that a one-particle picture emerges. *Molecular orbitals* are constructed as a first step in trying to describe these systems.

The Hückel Molecular Orbital Theory

As the “ π -electrons” in a molecule are less tightly bound than the remaining electrons, they may be approximated as electrons moving independently in a field provided by the remaining charges in the molecule. If there are N atoms in a molecule that contribute a $2p_z$ orbital to the π -system, the π -electron states may be pictured as “linear combinations of atomic orbitals” (LCAO),

$$\psi = \sum_{n=1}^N c_n \phi_n. \quad (10)$$

The ϕ_n are “pictured” as $2p_z$ orbitals, but more realistically they are energy eigenstates of an electron moving in the field of the remaining charges of the molecule localized at atom n .

The ψ of (10) describes a single electron. That is, there is an implicit assumption that the Hamiltonian has π -electron contributions that can be separated from all the remaining terms. Such states would be the eigenstates of some one-particle Hamiltonian. Hückel assumed that there was such a Hamiltonian and gave rules for determining this Hamiltonian in the basis set made up of $2p_z$ atomic orbitals: It is simply *assumed* that there is an orthonormal basis set $\{\phi_n\}_{n=1}^N$ in which the matrix elements of \hat{H} are

$$H_{ij} = \begin{cases} \alpha & \text{if } i = j, \\ \beta & \text{if } (i, j) \text{ are neighbors,} \\ 0 & \text{otherwise.} \end{cases}$$

Here “ α ” is the energy of an electron in an isolated ϕ_n state and “ β ” is a contribution to the energy of an electron from the attraction to nearby nucleus. If a free electron has energy = 0, then $\alpha, \beta < 0$.

If ϕ_1, \dots, ϕ_4 are the local ' $2p_z$ ' orbitals encountered as one moves around the ring in cyclobutadiene, the HMO Hamiltonian for the π electrons in this basis set is

$$H = \begin{bmatrix} \alpha & \beta & 0 & \beta \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ \beta & 0 & \beta & \alpha \end{bmatrix}.$$

The energy eigenvalues are (in ascending order) $\alpha + 2\beta, \alpha, \alpha, \alpha - 2\beta$. The ground state has two electrons with energy $\alpha + 2\beta$ and two with energy α . Spectroscopic excitation requires energy $2|\beta|$.

Rather than try to identify what approximations of the real Hamiltonian lead to separable contributions associated with the π electrons, Hückel simply identified α and β empirically. This was the first *empirical molecular orbital* theory. One finds, for example, a good prediction of the first absorption of a molecule's π -system with

$$\beta = -2.71\text{eV or } -21,900\text{cm}^{-1}$$

Closer comparison with experiment suggests that *different* values for these parameters are required in non-ring structures or in the identification of molecular heats of formation.

An extended Hückel molecular orbital theory

In the mid-1960's, the Hückel model was extended to give a more complete empirical molecular orbital characterization of a molecule. The extension consisted of

1. the inclusion of all *valence* electrons. C_4H_4 , for example, is pictured as containing 20 electrons, one from each H -atom and 4 from each C -atom, in atomic orbitals roughly associated with the $1s$ orbital of each H and the $2s, 2p_x, 2p_y$, and $2p_z$ orbitals of each C .

